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**Short Communication** 

## Morphology effect of MnO2 promoter to the catalytic performance of Pt toward methanol electrooxidation reaction



Yuan-Yuan Feng\*, Gui-Hua Song, Qiang Zhang, Jian-Ning Lv, Xi-Yu Hu, Yu-Long He, Xin Shen

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Three  $MnO_2$  samples with different well-defined morphologies including nanoplates, nanorods and corallines are prepared through a simple chemical precipitation method and used as the promoter/support for Pt electrocatalysts (denoted as  $PUMnO_2$ -P,  $PVMnO_2$ -R and Pt/MnO2-C, respectively). The morphology effects of MnO2 to the catalytic properties of Pt for methanol oxidation reaction (MOR) are intensively investigated. Results show that the catalytic properties of Pt are strongly dependent on the morphology of the promoter. Pt/MnO<sub>2</sub>-R with MnO<sub>2</sub> nanorods as the promoter shows the highest catalytic properties among the MnO<sub>2</sub>-promoted catalysts. The mass-specific activity and intrinsic activity of Pt in PVMnO<sub>2</sub>-R catalyst is  $0.51 \text{ A mg}^{-1}_{R}$  and  $11.54 \text{ A m}^{-2}_{Pl}$ , which is  $\alpha$ . 1.89 and 2.18 times that of commercial Pt/C catalysts  $(0.27 \text{ A mg}^{-1}_{R} \text{ and } 5.29 \text{ A m}^{-2}_{R})$ , respectively. Change in the electronic structure of Pt is responsible for the enhancement in the catalytic properties

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#### Introduction

Keymords

Methanol electrooxidation reaction (MOR) is of vital importance in the fields of energy conversion such as direct methanol fuel cells (DMFCs) [1]. Up to now, the most efficient catalyst for MOR is carbon-supported Pt materials [2]. However, the carbon material is prone to be oxidized under high potential and the intermediates such as CO formed during MOR are always adsorbed on the surface of Pt, leading to an obvious depression in the catalytic performances of Pt. Over the past decades, numbers of reports aimed at the

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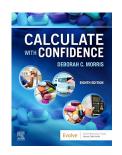
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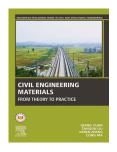
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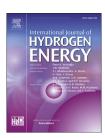




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#### ABSTRACT

Three  $MnO_2$  samples with different well-defined morphologies including nanoplates, nanorods and corallines are prepared through a simple chemical precipitation method and used as the promoter/support for Pt electrocatalysts (denoted as Pt/MnO<sub>2</sub>–P, Pt/MnO<sub>2</sub>-R and Pt/MnO<sub>2</sub>–C, respectively). The morphology effects of MnO<sub>2</sub> to the catalytic properties of Pt for methanol oxidation reaction (MOR) are intensively investigated. Results show that the catalytic properties of Pt are strongly dependent on the morphology of the promoter. Pt/MnO<sub>2</sub>-R with MnO<sub>2</sub> nanorods as the promoter shows the highest catalytic properties among the MnO<sub>2</sub>-promoted catalysts. The mass-specific activity and intrinsic activity of Pt in Pt/MnO<sub>2</sub>-R catalyst is 0.51 A mg<sup>-1</sup><sub>Pt</sub> and 11.54 A m<sup>-2</sup><sub>Pt</sub>, which is ca. 1.89 and 2.18 times that of commercial Pt/C catalysts (0.27 A mg<sup>-1</sup><sub>Pt</sub> and 5.29 A m<sup>-2</sup><sub>Pt</sub>), respectively. Change in the electronic structure of Pt is responsible for the enhancement in the catalytic properties of Pt/MnO<sub>2</sub>-R.

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#### Introduction

Methanol electrooxidation reaction (MOR) is of vital importance in the fields of energy conversion such as direct methanol fuel cells (DMFCs) [1]. Up to now, the most efficient catalyst for MOR is carbon-supported Pt materials [2]. However, the carbon material is prone to be oxidized under high potential and the intermediates such as CO formed during MOR are always adsorbed on the surface of Pt, leading to an obvious depression in the catalytic performances of Pt. Over the past decades, numbers of reports aimed at the

development of Pt-based bi/multi-metallic electrocatalysts such as PtRu, PtCu, PtNi and PtAu [3–8]. The promoter Ru can dissociate  $\rm H_2O$  molecules at much lower potentials than Pt to yield  $\rm -OH_{ads}$  species, which can oxidize the neighboring adsorbed CO molecules on the Pt surface. The Ni oxides can act as the oxygen donors for MOR and the alteration in the electronic structure enhances the rates of oxidation process. Owing to the bifunctional mechanism or electronic effects, the catalytic performances of PtM catalysts can thus be improved.

As another kind of efficient promoter, metal oxides have recently drawn wide attention because of their distinct

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advantages such as low cost, environment friendly and high stability [9-14]. For example, it is reported that ceria could remarkably enhance the catalytic properties of Pt for the electrooxidation of small-molecule alcohols, in terms of the activities and anti-poisoning ability, due to synergistic effect [9]. Xing and co-workers reported that Sb-doped tin dioxide could be used as an efficient promoter as well as a desired support for Pt catalysts because of its satisfactory electrical conductivity [10]. In our previous work, we found that Indoped tin dioxide could act as not only an efficient promoter but also a functionalized support for Pt [11], and Fe<sub>2</sub>O<sub>3</sub> with well-defined morphology could also act as efficient promoters to Pt and the morphology effects of Fe<sub>2</sub>O<sub>3</sub> were crucial to the catalytic properties of Pt [12]. For the series of Pt/Fe<sub>2</sub>O<sub>3</sub> catalysts, Pt/Fe<sub>2</sub>O<sub>3</sub>-R with Fe<sub>2</sub>O<sub>3</sub> nanorods as the promoter presents higher catalytic properties than that with Fe<sub>2</sub>O<sub>3</sub> nanoplates as the promoter, suggesting the presence of the morphology effects of the promoters.

In the past several years, the preparation and applications of manganese oxides (MnO<sub>x</sub>) have been widely reported since this kind of metal oxide has alterable valence and high stability in acidic media [15-19]. It is reported that Pt/MWCNTs catalyst using manganese oxide deposited on MWCNTs shows enhanced MOR activity as compared with Pt/MWCNTs catalyst [15]. MnO2 modified Pt/C catalyst shows more negative onset potential of MOR and much lower charge transfer resistance than Pt/C catalyst [16]. Manganese oxides with different morphologies show high activity and good stability for oxygen evolution reaction [17]. For the Pt-based electrocatalysts, morphology effects of the active species such as Pt have attracted much attention while few reports focused on the structural effects of the promoter. Since the catalytic properties of Pt are greatly dependent on the interfaces between the promoter/support and Pt, the surface structure of the promoter would be crucial for the improvement of the promotion effect. Rationally tuning the morphology of metal oxide promoters would have an important effect on the catalytic properties of Pt catalysts. Enlightened by the above findings and insights, we focused on the preparation of MnO2 nanocrystals with well-defined morphology and the investigation on their morphology effects in this work. The MnO2 nanocrystals include nanoplates, corallines and nanorods, which were used as the support/promoter for Pt catalysts (denoted as Pt/MnO<sub>2</sub>-P, Pt/MnO<sub>2</sub>-C and Pt/MnO<sub>2</sub>-R, respectively) for MOR. Results show that MnO2 can act as a favorable support and promoter for Pt electrocatalyst and the catalytic properties of Pt are closely related to the morphologies of MnO<sub>2</sub>. Among the three MnO<sub>2</sub> nanocrystals, Pt/MnO<sub>2</sub>-R with MnO<sub>2</sub> nanorods as the promoter shows the highest catalytic properties of Pt.

## **Experimental**

## Preparation of $MnO_2$ nanoplates, nanorods and nanocorallines

 $MnO_2$  nanoplates were synthesized through a simple precipitation method.  $MnSO_4 \cdot H_2O$  (1.7484 g) and  $KMnO_4$  (0.2724 g) were added in 25 mL of deionized water (80 °C). After vigorous

magnetic stirring for 30 min, 50 mL of deionized water (80 °C) was slowly added in the above mixture. Then, the mixture was kept stirring for 2 h at 80 °C. At last, the brown solid product was washed and dried in a vacuum oven for 12 h (60 °C). MnO<sub>2</sub> corals were synthesized using the similar process. The amount of KMnO<sub>4</sub> was still controlled at 0.2724 g, while the amount of MnSO<sub>4</sub>·H<sub>2</sub>O was changed to 0.4371 g. To prepare the MnO<sub>2</sub> nanorods, we altered the Mn precursor and used MnCl<sub>2</sub>·4H<sub>2</sub>O to replace MnSO<sub>4</sub>·H<sub>2</sub>O. MnCl<sub>2</sub>·4H<sub>2</sub>O (0.5400 g) was dissolved in 100 mL of isopropanol and sonicated for 30 min, then the mixture was slowly heated. Under vigorous stirring, 10 mL of KMnO<sub>4</sub> solution (0.20 M) was injected into the above mixture and kept refluxing for 30 min. After being cooled down to room temperature, the precipitate was filtered, washed and dried in a vacuum oven at 60 °C overnight.

## Preparation of Pt/MnO $_2$ -P, Pt/MnO $_2$ -C and Pt/MnO $_2$ -R samples

The preparation method of Pt colloids has been reported by our laboratory [20]: 10 mL of K<sub>2</sub>PtCl<sub>6</sub> solution (10.073 mM) and 16.80 mL sodium citrate solution (0.06 M) were mixed and diluted with distilled water to 150 mL. After stirring for 15 min, 6.67 mL NaBH<sub>4</sub> aqueous solution (0.045 M) was added in the mixture to prepare brown Pt colloid. The Pt colloid was placed in refrigerator for 12 h to let NaBH<sub>4</sub> completely hydrolyze. On the next day, 29.5 mg MnO<sub>2</sub> nanocrystal was added in the above Pt colloid. The pH of the solution was tuned to 12 and kept stirring for 8 h. Finally, the precipitate was filtrated, washed and dried overnight to obtain Pt/MnO<sub>2</sub> samples. For the three Pt/MnO<sub>2</sub> samples, the nominal loading of Pt was ca. 40 wt%.

## Physico-chemical characterizations of the $Pt/MnO_2$ samples

The morphology of the Pt/MnO<sub>2</sub> samples was characterized with field-emission scanning electron microscopy (SEM, JSM 7401 F, JEOL, Tokyo, Japan) with the operating voltage at 3.0 kV and JEM-2010 transmission electron microscope (TEM) operating at 120 kV. Bruker D8-Advance X-ray diffractometer (Germany) with Cu K $\alpha$  (wavelength = 0.15406 nm) as the radiation source was used to identify the catalyst crystalline. The scan rate was controlled at  $4^{\circ}$  min<sup>-1</sup> and the  $2\theta$  ranged from 20° to 80°. An X-ray photoelectron spectrometer (XPS) Thermo ESCALAB 250 with Al K $\alpha$  (h $\nu$  = 1486.6 eV) as the radiation source was chosen to confirm the surface composition and the chemical valence of Pt. Inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer Optima-4300DV Spectrometer) was used to determine the actual loading amount of Pt in the Pt/MnO<sub>2</sub> samples. For the Pt/MnO<sub>2</sub>-P, Pt/MnO<sub>2</sub>-R and Pt/MnO<sub>2</sub>-C samples, the real Pt loadings were 33.8 wt%, 33.6 wt% and 36.9 wt%, respectively. The Johnson Matthey Pt/C catalyst (20 wt% on carbon powder) was used as the reference.

## Electrochemical measurements

The working electrode used in this work was the traditional glassy carbon electrode (d = 5 mm). Prior to each use, the

electrodes were polished with 0.2–0.5 and 0.02–0.05  $\mu m$  alumina slurries. Pt/MnO<sub>2</sub> sample (5.0 mg) mixed with isopropanol (1.0 mL) to form the catalyst ink. 10  $\mu L$  of the ink was dropped onto the surface of the electrode with a microsyringe. After the suspension was dried under an infrared lamp, 10  $\mu L$  of Nafion solution (0.05 wt%, Dupont) was dropped onto the electrode and air-dried. The mass of Pt on the electrode was calculated from the real Pt loading data measured through ICP technique. For the Pt/MnO<sub>2</sub>–P, Pt/MnO<sub>2</sub>–R, Pt/MnO<sub>2</sub>–C and commercial Pt/C samples, the mass of Pt on the electrode was 16.9, 16.8, 18.4 and 10.0  $\mu g$ , respectively.

CHI 760E electrochemical workstation (Shanghai Chenhua Apparatus, China) was used to carry out the electrochemical measurements. Saturated calomel electrode (SCE) was chosen as the reference electrode and platinum plate electrode (1.0 cm  $\times$  1.0 cm) was the auxiliary electrode. In the present work, all of the following mentioned potentials were referred to SCE. Electrochemical techniques including cyclic voltammetry (CV) and chronoamperometry (CA) were performed in  $H_2SO_4$  (0.5 M) containing  $CH_3OH$  (2.0 M) solution. Prior to each electrochemical measurement, the solution was purged with high-purity dry  $N_2$  to remove the dissolved  $O_2$ . The CA measurements were carried out at a constant potential of 0.50 V vs. SCE.

## Results and discussion

#### Characterizations of the Pt-MnO<sub>2</sub>/C samples

Fig. 1 shows the SEM and TEM images of MnO<sub>2</sub> nanocrystals and Pt/MnO2 samples. It can be seen the morphology of the three MnO<sub>2</sub> samples was quite different. When MnSO<sub>4</sub>·H<sub>2</sub>O was used as the Mn precursor, the morphology of MnO<sub>2</sub> was nanoplates and nanocorals; while MnSO4·H2O was replaced with MnCl<sub>2</sub>·4H<sub>2</sub>O, MnO<sub>2</sub> nanorods were obtained. The size of the nanoplates (Fig. 1A, D) is uniform and around 50 nm. The nanorods (Fig. 1B, E) are about 20 nm across and 100-200 nm long. Fig. 1C and F shows the coral nanostructure of MnO2 with a rough surface. After the deposition of Pt nanoparticles, no evident change of the morphology is observed for the MnO2 supports. The enlarged images of the deposited Pt nanoparticles on the supports are shown in the inset of Fig. 1D-F and the Pt nanoparticle size distributions are shown in Fig. 1H–J. It can be seen that these Pt nanoparticles are almost spherical and have a well deposition state. The average particle sizes of Pt in Pt/MnO<sub>2</sub>-P, Pt/MnO<sub>2</sub>-R and Pt/MnO<sub>2</sub>-C samples are ca. 3.21, 2.98 and 2.99 nm, respectively, which were evaluated from an ensemble of at least 300 particles in an arbitrarily chosen area of the corresponding TEM images. Fig. 1G shows the EDS spectrum of the representative Pt/ MnO<sub>2</sub>-P sample. The peaks corresponding to Pt, Mn and O were obvious, besides them, other elements such as C and Cu were also detected. Apparently, the signals of Cu arose from the copper mesh and the signal of C originated from the supporting film of the copper mesh.

Fig. 2 gives the XRD patterns of the  $MnO_2$  and  $Pt/MnO_2$  samples. For the three different  $MnO_2$  nanocrystals, the diffraction peaks at  $2\theta = 28.9^{\circ}$ ,  $37.5^{\circ}$ ,  $41.9^{\circ}$ ,  $49.9^{\circ}$ ,  $60.2^{\circ}$  and  $65.2^{\circ}$  are associated with the (310), (211), (301), (411), (521) and (002) crystal planes of  $MnO_2$  (PDF#44–0141). After the deposition of

Pt nanoparticles, besides the signals from  $MnO_2$ , other significant peaks at around 39.8°, 46.2° and 67.4° corresponding to the (111), (200) and (220) crystal planes of Pt were also found for all of the samples (PDF#04-0802), indicating the successful deposition of Pt nanoparticles on the surface of  $MnO_2$  supports. Generally, the Debye-Scherrer equation can be used to calculate the average crystallite sizes of the catalysts. In Fig. 2, it can be seen that the strongest peak of polycrystalline Pt emerged at 39.8°, which was overlapped by the (211) crystal plane of  $MnO_2$ . To avoid the disturbance of the diffraction signals of  $MnO_2$ , we did not use Scherrer equation to calculate the crystallite size of Pt in this work.

XPS technique was used to characterize the chemical states of Pt and the surface composition of the samples. Fig. 3A-C shows the Pt XPS spectra and Fig. 3D exhibits the entire XPS spectra of the Pt/MnO<sub>2</sub> samples. In Fig. 3A-C, the Pt 4f signals can be deconvoluted into two doublets, the more intensive doublet with binding energies (BEs) at ca. 71.5 and 74.8 eV comes from the signature of Pt (0), and the relatively weak doublet with binding energies at ca. 72.4 and 75.6 eV corresponds to the signatures of Pt (II). Compared with the Pt (0) and Pt (II) positions of pure Pt/C catalyst [21], the BEs of Pt  $\,$ XPS spectra shifted to higher values by 0.5 eV, which suggests the presence of electronic interaction between Pt and the metal oxide support and this electronic interaction would alter the electronic structures of Pt [22,23]. In addition, on carefully observing the doublets, we found that there was slight shift (0.1–0.2 eV) of Pt (0)4 $f_{7/2}$  and 4 $f_{5/2}$  for Pt/MnO<sub>2</sub>-R sample. That is, its BEs showed a little bit high values (ca. 71.6 and 74.9 eV), as compared with those of the other two Pt/MnO<sub>2</sub> samples (ca. 71.5 and 74.8 eV). This weak shift of Pt is primarily a manifestation of a more significant electronic effect between Pt and MnO<sub>2</sub> support for Pt/MnO<sub>2</sub>-R sample.

#### Electrochemical behaviors of the Pt/MnO<sub>2</sub> samples

Cyclic voltammograms of  $Pt/MnO_2$  samples in  $H_2SO_4$  electrolyte (0.5 M)

Fig. 4 gives the cyclic voltammograms of the Pt/MnO $_2$  samples in H $_2$ SO $_4$  solution (0.5 M) without methanol. The profiles of the three Pt/MnO $_2$  samples are almost identical. The reduction peaks at around 0.58 V are associated with the reduction process of oxidized Pt produced in the forward scan to the high potential limit. In the relatively low potential region of the CV curves, the reduction/oxidation signals from -0.2 to 0.1 V generally came from the ad/desorption of atomic H on the surface of Pt atoms [2]. According to the well-accepted stoichiometry (H:Pt = 1:1) of H adsorbed on the surface of polycrystalline Pt, the electrochemically active surface area (EAS) data of Pt in the Pt/MnO $_2$  samples can thus be calculated from the coulombic charges related with the ad/desorption process of H atoms. The equation is described as follows [24,25]:

$$EAS = (Q_H/Q_e)A_{Pt}/W_{Pt}$$
 (1)

where  $Q_H$  is the charge expended for the electro-oxidative desorption of atomic H on the surface of Pt, which is equal to the calibrated area of anodic H peaks on the positive-going scan of the voltammograms;  $Q_e$  is the elementary charge

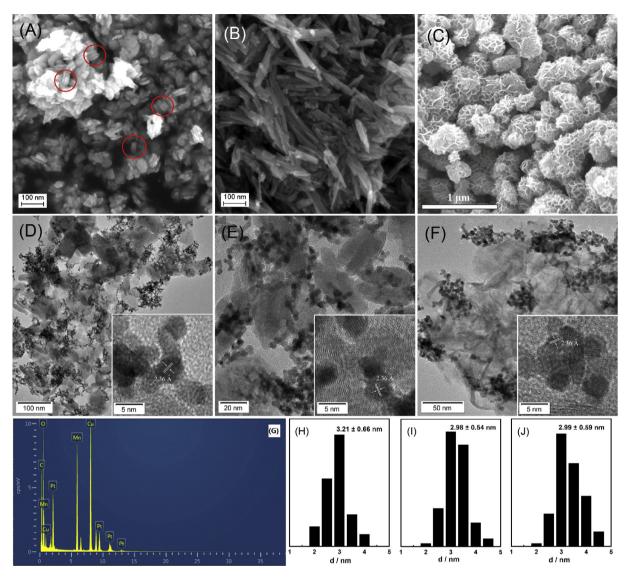


Fig. 1 – Representative SEM images of  $MnO_2$ –P(A),  $MnO_2$ -R(B) and  $MnO_2$ –C(C); TEM images of  $Pt/MnO_2$ –P(D),  $Pt/MnO_2$ -R(E) and  $Pt/MnO_2$ –C(F). The corresponding size histograms for the metal particles are shown in the bar-graph (H-J). Fig. 1G shows the EDS spectrum of the representative  $Pt/MnO_2$ –P sample.

 $(1.602 \times 10^{-19} \text{ C})$ ;  $A_{Pt}$  is the exposed area of a Pt atom  $(0.077 \text{ nm}^2, \text{this data was obtained from the atomic density for polycrystalline Pt surface: <math>1.3 \times 10^{15} \text{ cm}^{-2}$ ), and  $W_{Pt}$  refers to the mass of Pt on the carbon electrode. Therefore, the above equation can be rewritten as:

EAS 
$$(m^2) = Q_H/(0.21 \times W_{Pt})$$
 (2)

Based on Eq. (2), the calculated EAS data of Pt/MnO<sub>2</sub>–P, Pt/MnO<sub>2</sub>–R, Pt/MnO<sub>2</sub>–C and Pt/C samples are 40.4, 44.2, 34.8 and  $51.0~\rm m^2~g^{-1}_{Pt}$ , respectively. Generally, the EAS data are strongly dependent on the size of the metal particles. The smaller the particle size, the higher the EAS of Pt in the samples. However, the EAS data of the three samples did not obey the general rule. The particle sizes of Pt in Pt/MnO<sub>2</sub>–R and Pt/MnO<sub>2</sub>–C catalysts are comparable (2.98 and 2.99 nm), while the EAS data of the latter is about  $10~\rm m^2~g^{-1}_{Pt}$  lower than that of the

former. This phenomenon is probably related to the aggregation of the Pt NPs in Pt/MnO $_2$ –C sample. In addition, for the three Pt/MnO $_2$  catalysts, the changed trend of the H ad/desorption peak areas agree well with the reduction peaks of Pt oxide at 0.53 V and higher exposed surface area of Pt induced stronger reduction peak of Pt oxide. The arrows in Fig. 4 indicated the changed trend.

Methanol electro-oxidation behaviors on Pt/MnO $_2$  catalysts Fig. 5 gives the MOR results on the Pt/MnO $_2$ –P, Pt/MnO $_2$ –R and Pt/MnO $_2$ –C catalysts in 0.5 M H $_2$ SO $_4$  + 2.0 M CH $_3$ OH solution. For a rigorous evaluation of the catalyst activities, the currents of methanol oxidation have been normalized to the mass of Pt on the working electrode to give the mass-specific activity (MSA) of the catalysts. From Fig. 5, it is seen that the three Pt/ MnO $_2$  catalysts exhibited two well-defined oxidation peaks in

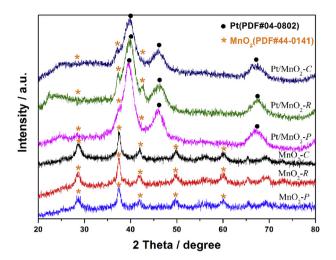


Fig. 2 – XRD diffraction patterns of  $MnO_2$ –P,  $MnO_2$ -R,  $MnO_2$ –C and the corresponding  $MnO_2$ -supported Pt samples. The diffraction peaks marked with dot and star correspond to the signals of Pt (PDF#04–0802) and  $MnO_2$  (PDF#44–0141), respectively.

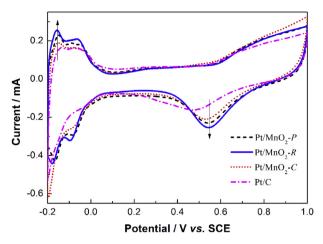


Fig. 4 – Cyclic voltammograms of the Pt/MnO $_2$  and Pt/C catalysts in 0.5 M H $_2$ SO $_4$  solution without methanol. For the Pt/MnO $_2$ -P, Pt/MnO $_2$ -R, Pt/MnO $_2$ -C and Pt/C samples, the mass of Pt on the working electrode was 16.9, 16.8, 18.4 and 10.0 µg, respectively. Scan rate: 20 mV s $^{-1}$ .

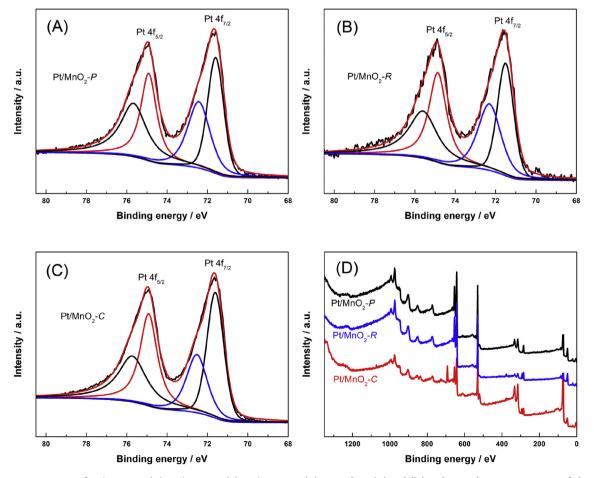


Fig. 3 - XPS spectra of Pt/MnO<sub>2</sub>-P(A), Pt/MnO<sub>2</sub>-R(B), Pt/MnO<sub>2</sub>-C(C) samples. (D) Exhibits the entire XPS spectra of the samples.

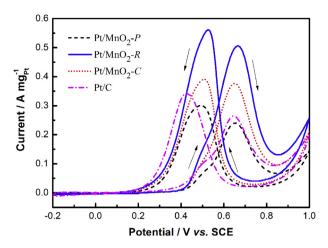


Fig. 5 - Cyclic voltammograms of Pt/MnO $_2$  and Pt/C catalysts in 0.5 M  $\rm H_2SO_4 + 2.0$  M  $\rm CH_3OH$  solution.

the positive and negative-going scans. Both peaks are related to the electro-oxidation behaviors of methanol [26]. The three Pt/MnO<sub>2</sub> catalysts exhibit comparable onset potential of MOR, while the currents of MOR are quite different. Among the catalysts, Pt/MnO2-R shows the highest MSA. The peak current of Pt/MnO<sub>2</sub>-R is 0.51 A  $mg^{-1}_{Pt}$ , which is about 1.89, 2.12 and 1.34 times that of Pt/C (0.27 A  $mg^{-1}_{Pt}$ ), Pt/MnO<sub>2</sub>-P (0.24 A  $mg^{-1}_{Pt}$ ) and Pt/MnO<sub>2</sub>-C (0.38 A  $mg^{-1}_{Pt}$ ) catalysts, respectively. The currents of methanol oxidation have been normalized to the mass of Pt on the electrode, however, the exposed surface area of Pt atoms in the three catalysts are different. Therefore, the comparison of the MOR currents normalized to the EAS of Pt would be more significative. That is, the intrinsic activities (IA) of Pt in the catalysts should also be used to evaluate the catalytic performances of the three Pt/MnO2 catalysts. Based on the above EAS data of Pt, the IA data of the three Pt/MnO<sub>2</sub> catalysts are thus calculated and listed in Table 1. It can be seen that all of the Pt/MnO2 catalysts show higher IA than commercial Pt/C catalyst, suggesting the promotion effects of MnO<sub>2</sub> on Pt catalyst for MOR. The IA data of Pt/MnO<sub>2</sub>-C (10.91 A m<sup>-2</sup><sub>Pt</sub>) is comparable to that of Pt/MnO<sub>2</sub>-R (11.54 A m<sup>-2</sup><sub>Pt</sub>) which has the highest IA data among the Pt/MnO<sub>2</sub> catalysts. For Pt/MnO<sub>2</sub>-R catalyst, the IA is ca. 1.94 and 2.18 times that of Pt/MnO<sub>2</sub>-P (5.94 A m<sup>-2</sup> Pt) and Pt/C (5.29 A m<sup>-2</sup> Pt) catalysts, respectively. Both MSA and IA results suggest that MnO2 nanorods present more positive promotion effects to Pt catalysts. Combined with the above XPS results, we think the change in the electronic structure of Pt arising from the electronic interaction between Pt and the oxide support should be responsible for the enhanced catalytic activities [27]. The binding energies of Pt4f with higher values suggested a

Table 1 — Electrochemical parameters for methanol<br/>electro-oxidation on Pt/MnO2 and Pt/C catalysts.CatalystsEAS  $(m^2 g^{-1}_{Pt})$ MSA  $(A mg^{-1}_{Pt})$ IA  $(A m^{-2}_{Pt})$ Pt/MnO2-P40.40.245.94Pt/MnO2-R44.20.5111.54

0.38

0.27

10.91

5.29

34.8

51.0

Pt/MnO<sub>2</sub>-C

Pt/C

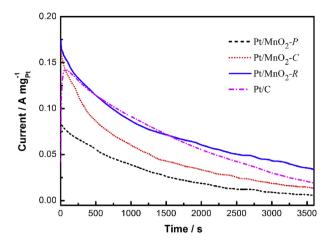


Fig. 6 – Chronoamperograms of Pt/MnO<sub>2</sub> and Pt/C catalysts in 0.5 M  $H_2SO_4 + 2.0$  M  $CH_3OH$  at 0.50 V.

downshift of the *d*-band center of Pt, leading to a depressed interaction between Pt and the CO-like intermediate species produced during the MOR process. Therefore, among the three Pt/MnO<sub>2</sub> catalysts, Pt/MnO<sub>2</sub>-R catalyst with MnO<sub>2</sub> nanorods as the support exhibits the highest catalytic activity for MOR.

Besides the catalytic activity, the long-term stability of a catalyst is also an essential factor for evaluating the suitability for the real application of the catalysts. Fig. 6 shows the chronoamperometric curves of the three MnO2-supported Pt catalysts in the electrolyte of H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>OH at 0.50 V. This potential was chosen in the range from the open circuit potential to the peak potential shown in Fig. 5. It is seen that all of the Pt/MnO2 catalysts showed gradual decrease in the current especially in the first 20 min, which may arise from the poisoning of the intermediate species such as the adsorbed CO and COOH formed during the process of MOR [28,29]. As times goes by, the current decayed slowly. For Pt/MnO<sub>2</sub>-R catalyst, the initial and limit currents of methanol oxidation were 0.170 and 0.034 A  $mg^{-1}_{Pt}$ , respectively. Both currents were much higher than those on the Pt/MnO<sub>2</sub>-P (0.083 and  $0.006 \text{ A mg}^{-1}_{Pt}$ ) and Pt/MnO<sub>2</sub>-C (0.165 and 0.014 A mg<sup>-1</sup><sub>Pt</sub>) catalysts, indicating much higher catalytic properties of Pt/ MnO<sub>2</sub>-R for MOR. As compared with commercial Pt/C catalyst, the initial and limit currents of Pt/MnO<sub>2</sub>-R were also higher. However, it is also found that although the current decay of Pt/  $MnO_2$ -R (ca. 79%) was much lower than that on Pt/MnO<sub>2</sub>-P (ca. 92%), Pt/MnO<sub>2</sub>-C (ca. 91%) and Pt/C (ca. 85%) catalysts, Pt/ MnO<sub>2</sub>-R still lost nearly 80% current in the 3600 s. Further work is needed to improve the catalytic stability of the catalysts in the real application for DMFCs.

#### **Conclusions**

The present work reports the promotion effect of MnO<sub>2</sub> support with different morphologies on the catalytic performance of Pt. Our data clearly demonstrate the catalytic performances of Pt toward MOR are closely related to the morphology of the MnO<sub>2</sub> support. Among the three MnO<sub>2</sub>-supported Pt catalysts, Pt/MnO<sub>2</sub>-R with MnO<sub>2</sub> nanorods as the support and promoter exhibits the highest mass-specific and intrinsic activities. The

MnO<sub>2</sub> support with different morphologies produces different interaction between Pt and MnO<sub>2</sub>, and thus alters the electronic structure of Pt, which is favorable for enhancing the catalytic properties of Pt/MnO<sub>2</sub>-R catalyst.

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# Exploring the Variety of Random Documents with Different Content

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## THE INTRODUCTION.

Before we enter on our present undertaking, we shall premise a few things leading to the subject matter thereof; and that we may begin with what is most obvious, let it be considered,

- I. That it is a duty incumbent on all who profess the Christian name, to be well acquainted with those great doctrines on which our faith, hope, and worship are founded; for, without the knowledge hereof, we must necessarily be at a loss as to the way of salvation, which none has a right to prescribe, but he who is the author thereof.<sup>[3]</sup>
- II. This knowledge of divine truth must be derived from the holy scriptures, which are the only fountain of spiritual wisdom, whereby we are instructed in those things that could have been known no other way, but by divine revelation.
- III. It will be of singular use for us not only to know the doctrines that are contained in scripture; but to observe their connexion and dependence on one another, and to digest them into such a method, that subsequent truths may give light to them that went before; or to lay them down in such a way, that the whole scheme of religion may be comprised in a narrow compass, and, as it were, beheld with one view, which will be a very great help to memory: and this is what we call a system of divine truths, or a methodical collection of the chief articles of our religion, adapted to the capacity of those who need to be taught the first principles of the oracles of God: and if they are designed to give the world a specimen of that form of sound words, which the church thinks itself obliged to hold fast, and stedfastly to adhere to, then we call it a confession of faith; or, if digested into questions and answers, we call it a catechism. And

though systems of divinity, confessions of faith, and catechisms, are treated with contempt, instead of better arguments, by many who are no friends to the doctrines which they contain, and who appear to be partial in their resentment, in as much as they do not dislike those treatises which are agreeable to their own sentiments, by whatever name they are called; yet we are bound to conclude that the labours of those who have been happy in the sense they have given of scripture, and the method in which they have explained the doctrines thereof, in what form soever they have been, are a great blessing to us; though we are far from concluding that they are of equal authority with scripture, or that every word which they use is infallible; nor do we regard them any farther than as they are agreeable to, or sufficiently proved from scripture.

IV. Confessions of faith and catechisms are not to be reckoned a novel invention, or not consonant to the scripture rule, since they are nothing else but a peculiar way of preaching or instructing us in divine truths. Therefore, since scripture lays down no certain invariable rule concerning this matter, the same command that warrants preaching the word in any method, includes the explaining of it, as occasion serves, in a catechetical one.

V. As there are many excellent bodies of divinity printed in our own and foreign languages, and collections of sermons on the principal heads thereof; so there are various catechisms, or methodical summaries of divine truths, which, when consonant to scripture, are of great advantage to all Christians, whether elder or younger.

VI. The catechisms composed by the Assembly of Divines at Westminster, are esteemed as not inferior to any that are extant, either in our own or foreign languages, the doctrines therein contained being of the highest importance, and consonant to scripture; and the method in which they are laid down is so agreeable, that it may serve as a directory for the ranging our ideas of the common heads of divinity in such an order, that what occurs under each of them may be reduced to its proper place. It is the larger of them that we have attempted to explain and regulate our

method by; because it contains several heads of divinity not touched on in the shorter. And if, in any particular instance, we are obliged to recede from the common mode of speaking, (though it is to be hoped not from the common faith, once delivered to the saints) we submit our reasoning to the judgment of those who are disposed to pardon less mistakes, and improve what comes with sufficient evidence to the best purposes.

The work indeed is large, but the vast variety of subjects will render it more tolerable; the form in which it appears is somewhat differing from that in which it was first delivered, in a public audience, though that may probably be no disadvantage to it, especially since it is rather designed to be read in families than committed to memory, and repeated by different persons, as it has been. The plainness of the style may contribute to its usefulness; and its being less embarrassed with scholastic terms than some controversial writings are, may render it more intelligible to private Christians, whose instruction and advantage is designed thereby. It would be too great a vanity to expect that it should pass through the world without that censure which is common to all attempts of the like nature, since men's sentiments in divinity differ as much as their faces; and some are not disposed to weigh those arguments that are brought to support any scheme of doctrine, which differs from what they have before received. However, the work comes forth with this advantage, that it has already conflicted with some of the difficulties it is like to meet with, as well as been favoured with some success, and therefore the event hereof is left in his hand whose cause and truth is endeavoured to be maintained.

## Quest. I.

QUEST. I. What is the chief and highest end of man?

Answ. Man's chief and highest end is to glorify God, and fully to enjoy him for ever.

- 1. It is supposed, in this answer, that every intelligent creature, acting as such, designs some end, which excites endeavours to attain it.
- 2. The ends for which we act, if warrantable, may be considered as to their degree of excellency, and, in proportion to it, are to be pursued by proper means conducing thereto.
- 3. There is one that may be termed the chief and highest end, as having an excellency and tendency to make us blessed above all others: this consists, as it is observed in this answer, in the glorifying and eternal enjoyment of God, the fountain of blessedness.

If it be enquired with what propriety these may both be called chief and highest, the answer is obvious and easy, *viz.* That the former is absolutely so, beyond which nothing more excellent or desirable can be conceived; the latter is the highest or best in its kind, which, notwithstanding, is referred, as a means leading to the other; and both these ends, which, with this distinction, we call chief and highest, are to be particularly considered by us, together with the connexion that there is between them.<sup>[4]</sup>

I. We are to consider what it is to glorify God. In order to our understanding of this, let it be premised,

- 1. That there is a great difference between God's glorifying himself and our glorifying him; he glorifies himself when he demonstrates or shews forth his glory; we glorify him by ascribing to him the glory that is his due: even as the sun discovers its brightness by its rays, and the eye beholds it. God glorifies himself, by furnishing us with matter for praise; we glorify him when we offer praise, or give unto him the glory due to his name.
- 2. Creatures are said to glorify God various ways: some things do it only objectively, as by them, angels and men are led to glorify him; thus the heavens declare his glory, Psal. xix. 1. The same might be said of all other inanimate creatures which glorify God, by answering the end of their creation, though they know it not: but intelligent creatures, and particularly men, are said to glorify God actively; and this they do by admiring and adoring his divine perfections: these, as incomprehensible, are the object of admiration; and accordingly the apostle admires the divine wisdom, Rom. xi. 33. O the depth of the riches, both of the wisdom and knowledge of God; how unsearchable are his judgments, and his ways past finding out! and as they are divine, so they are the object of adoration: God is to be admired in all the displays of his relative or manifestative glory; and his work which men behold, is to be magnified, Job xxxvi. 24. But he is to be adored more especially for his essential perfections.

We are to glorify God, by recommending, proclaiming, and setting forth his excellency to others. What we have the highest value for, we desire that others may have the same regard to it with ourselves: thus it is observed by the evangelist, that when the disciples received their first conviction that Jesus was the Messiah, they imparted this to others; as Andrew to Peter, and Philip to Nathanael, John i. 41, 45. so the woman of Samaria being convinced hereof, endeavoured to persuade all her neighbours to believe in him, as she did, John iv. 28, 29. Thus we glorify God by making mention of his name with reverence, proclaiming his goodness with thankfulness, and inviting others, as the Psalmist does, Psal. xxxiv. 8. to taste and see that he is good.

But since this is a very comprehensive duty including in it the whole of practical religion, it may be considered under the following particulars.

- 1. We glorify God by confessing and taking shame to ourselves for all the sins we have committed, which is interpretatively to acknowledge the holiness of his nature, and of his law, which the apostle asserts to be *holy, just, and good*, Rom. vii. 12. This Joshua advises Achan to do; *to give glory to God, by making confession to him*, Josh. vii. 19. And thus the penitent thief, who was crucified with our Saviour, glorified God, by confessing that he received the *due reward of his deeds*, Luke xxiii. 40, 41. So did the Levites, in their prayer recorded by Nehemiah, when they said to God, *Thou art just in all that is brought upon us, for thou hast done right, but we have done wickedly*, Neh. ix. 33.
- 2. By loving and delighting in him above all things, which is to act as those who own the transcendent amiableness of his perfections, as the object of their highest esteem. Thus the Psalmist says, Psal. lxxiii. 25. Whom have I in heaven but thee; and there is none, or nothing, upon earth, that I desire besides thee.
- 3. By believing and trusting in him, committing all our concerns, both in life and death, for time and eternity, into his hands: thus Abraham is said *to be strong in faith, giving glory to God*, Rom. iv. 20. And the apostle Paul, 2 Tim. i. 12. to have *committed his all to him*.
- 4. By a fervent zeal for his honour; and that either for the honour of his truth and gospel, when denied, disbelieved, or perverted; or for the honour of his holiness, or any of his other perfections, when they are reflected on, or reproached, either by the tongues or actions of those who set themselves against him.
- 5. By improving our talents, and bringing forth fruit in proportion to the means we enjoy; *herein*, says our Saviour, *is my Father glorified*, that ye bear much fruit, John xv. 8.

- 6. By walking humbly, thankfully, and chearfully before God. Humility acknowledges that infinite distance which is between him and us; retains a due sense of our own unworthiness of all we have or hope for; and owns every thing we receive to be the gift of grace; *By the grace of God*, says the apostle, *I am what I am*, 1 Cor. xv. 10. Thankfulness gives him the glory, as the author of every mercy; and accordingly sets a due value on it, in that respect. And to walk chearfully before him, is to recommend his service as most agreeable, whereby we discover that we do not repent that we were engaged therein; which is what the Psalmist intends, when he says, Psal. c. 2. *Serve the Lord with gladness*.
- 7. By heavenly-mindedness; when we desire to be with him to behold his glory. To which we must add, that all this is to be done in the name of Christ, our great Mediator, and by strength derived from him.
- 8. As we are to glorify God, by yielding obedience to his commanding will, as in the aforesaid instances, so we are to do it by an entire submission to his disposing will; particularly, when under afflictive dispensations of providence, we must own his sovereignty and right to do what he will with us as his own, Matth. xx. 15. and that these afflictions are infinitely less than our iniquities deserve, Ezra ix. 13. And we must adore his wisdom and goodness in trying our graces hereby, and dealing with us in such a way as is needful, and that only for a season, 1 Pet. i. 6. And we are to own his goodness in suiting our strength to our burdens, and over-ruling all this for our spiritual advantage. It also consists in an easy, patient, and contented frame of spirit, without the least murmuring or repining thought; concluding, that whatever he does is well done, Psal. cxix. 65. And, which is something more, in rejoicing that we are counted worthy to suffer the loss of all things, yea, even of life itself, if called to it, for his sake; of which we have various instances in scripture, Acts v. 41. Heb. x. 34. Acts xx. 24.

Moreover, we ought to glorify God in all the natural, civil, and religious actions of life, which are to be consecrated or devoted to

him. We enjoy the blessings of life to no purpose if we do not live to the Lord, and thankfully acknowledge that we receive them all from his hand; and whatever the calling be, wherewith we are called, we must therein abide with him, and see that we have his warrant to engage in it, and expect success from his blessing attending it, or else it will be to no purpose. Thus says Moses, *It is the Lord thy God that giveth thee power to get wealth*, Deut. viii. 18. And, in all our dealings with men, we are to consider ourselves as under the inspection of the all-seeing eye of God, to whom we are accountable for all we do, and should be induced hereby, to exercise ourselves always to keep consciences void of offence towards God and man.

As for religious duties, wherein we have more immediately to do with God, we are to glorify him, by taking up a profession of religion in general, as being influenced by his authority, encouraged by his promised assistance, and approving ourselves to him, as the searcher of hearts: and we must take heed that we do not rest in an outward form or shew of godliness, without the power thereof; or in having a name to live without a principal of spiritual life, by which we may be enabled to put forth living and spiritual actions agreeable thereunto: and all these religious duties must be performed by faith, whereby we depend on Christ, our great Mediator, both for assistance and acceptance; by which means we glorify him, as the fountain of all grace, in whom alone both our persons and services are accepted in the sight of God, and redound to his glory. And this is to be done at all times; so that when our thoughts are not directly conversant about any of the divine perfections, as it often happens, when we are engaged in some of the more minute, or indifferent actions of life; yet we are to glorify him habitually, as having our hearts right with him; so that whatever we do may refer ultimately to his glory. As every step the traveller takes is toward his journey's end, though it may not be every moment in his thoughts; so the less important actions of life should be subservient to those that are of greater consequence, in which the honour of God and religion is more immediately concerned; in which sense we maybe said to glorify him therein.

Thus having considered, that it is our indispensable duty to make the glory of God our highest end in all our actions, we might farther add, as a motive to enforce it, that God is the first cause of all things, and his own glory was the end he designed in all his works, whether of creation or providence: and it is certain, that this is the most excellent end we can propose to ourselves; therefore the most valuable actions of life ought to be referred to it, and our hearts most set upon it; otherwise we act below the dignity of our nature; and, while other creatures, designed only to glorify him objectively, answer the end for which they were made, we, by denying him that tribute of praise which is due from us, abuse our superior faculties, and live in vain.

- II. The next thing to be considered is what it is to enjoy God.
- 1. This supposes a propriety in, or claim to him, as our God. We cannot be said to enjoy that which we have no right or claim to, as one man cannot be said to enjoy an estate which belongs to another; so God must be our God in covenant, or we cannot enjoy him; and that he is so, with respect to all that fear him, is evident, inasmuch as he gives them leave to say, Psal. xlviii. 14, This God is our God; and, Psal. lxvii, 6. God, even our God, shall bless us.
- 2. To enjoy God, is to have a special gracious communion with him, to converse or walk with him, and to delight in him; as when we can say, 1 John i. 3. *Truly our fellowship is with the Father, and with his Son Jesus Christ*. This enjoyment of God, or communion with him, is,
- (1.) That which we are blessed with in this world, which is but imperfect, as we know and love him but in part, and our communion with him is often interrupted and weakened, through the prevalency of indwelling sin: and that joy and delight which arises from thence is often clouded and sullied; and, at best, we enjoy him here but in a mediate way, in and under his ordinances, as agreeable to this present state.
- (2.) Believers shall enjoy him perfectly and immediately in heaven, without intermission or abatement, and that for ever; this is called,

Seeing him as he is, 1 John iii. 2. and being with him where he is, to behold his glory, John xvii. 24. And in order hereto, their souls shall be made capable or receptive hereof, by the removal not only of all sinful but natural imperfections, and shall be more enlarged, as well as have brighter discoveries of the divine glory: and this shall be attended with a perfect freedom from all the consequences of sin; such as sorrow, divine desertion, and the many evils that attend us in this present life; as well as from all temptations to it. So that their happiness shall be confirmed and secured to them, and that with this advantage, that it shall be impossible for them to be dispossessed of it. This is certainly the most desirable end, next to the glory of God, that can be intended or pursued by us.<sup>[5]</sup>

III. This leads us to consider the connexion that there is between our glorifying God and enjoyment of him. God has joined these two together, so that one shall not be attained without the other. It is the highest presumption to expect to be made happy with him for ever, without living to his glory here. For in as much as heaven is a state of perfect blessedness, they, who shall hereafter be possessed of it, must be trained up, or made meet for it; which is the grand design of all the means of grace. How preposterous would it be to suppose, that they, who have no regard to the honour of God here, shall be crowned with glory, honour, immortality, and eternal life, in his presence hereafter! Therefore a life of holiness is absolutely necessary to the heavenly blessedness; and since these two are so connected together, they who experience the one, shall not fail of the other; for this is secured to them by the faithfulness of God, who has promised to give grace and glory, Psal. lxxxiv. 11. Therefore, he who begins a good work in them, will perform it, Phil. i. 6. and give them the end of their faith, even the salvation of their souls, 1 Pet. i. 8.

From the connexion that there is between our glorifying and enjoying God, we may infer,

1. That it is a very preposterous thing for any one to assign this as a mark of grace, that persons must be content to perish eternally, that

God may be glorified. It is true, it is alleged in favour of this supposition, that Moses, and the apostle Paul, seem to give countenance to it; one by saying, Exod. xxxii. 32. *If thou wilt forgive their sin; and, if not, blot me, I pray thee, out of the book which thou hast written*; the other, Rom. ix. 3. *I could wish that myself were accursed from Christ, for my brethren and kinsmen according to the flesh.* 

But to this it may be answered, that Moses, in desiring to be blotted out of the book which God had written, must not be supposed to be willing to perish eternally for Israel's sake; but he is content to be blotted out of the book of the living, or to have his name no more remembered on earth; and seems to decline the honour which God had offered him, when he said, Exod. xxxii. 10. Let me alone, that I may consume them; and I will make of thee a great nation; he desires not the advancement of his own family, if Israel must cease to be a people, to whom God had promised to be a God.

As for the apostle Paul's wish, it is either, as some suppose, a rash and inconsiderate flight of zeal for God, and so not warrantable, though in some respects proceeding from a good principle; or rather, as I humbly conceive the meaning is, he could wish himself accursed from Christ, so far as is consistent with his love; or he is content to be under the external marks of God's displeasure; or deprived of the comfortable sensation of his love, or many of those fruits and effects thereof, which the believer enjoys in this life: for I cannot, in the least, think he desires to be deprived of a real interest in it, or to be eternally separated from Christ, on any condition whatsoever.<sup>[6]</sup>

2. Since the eternal enjoyment of God is one great end which we ought to have in view, it is no sign of a mercenary spirit to have an eye to the heavenly glory, to quicken us to duty; seeing this is promised by God to those who are faithful, thus, Psal. lxxxiii. 24. *Thou shalt guide me with thy counsel, and afterward receive me to glory*. The like promises we have in many other scriptures, which are designed to excite our desire and hope of this blessedness; therefore the exercise of these graces, from such motives, is far from being

unlawful: yea, it is commended in the saints, who are said, Heb. xi. 16. to *desire a better country, that is, an heavenly*. And Moses is commended for having the *recompence of reward* in view, when he preferred the *reproach of Christ* before the *treasures of Egypt*, ver. 26.

Nevertheless, when this respect to future blessedness is warrantable, it must be considered as an expedient for our glorifying God, while we behold his glory; and when we consider it as a reward, we must not look upon it as what is merited by our service, or conferred in a way of debt, but as a reward of grace, given freely to us, though founded on the merits of Christ.

## Quest. II.

QUEST. II. How doth it appear that there is a God?

Answ. The very light of nature in man, and the works of God, declare that there is a God; but his word and Spirit only, do sufficiently and effectually reveal him unto men for their salvation.

Before we enter on the proof of this important doctrine, let it be premised, that we ought to be able to prove by arguments, or give a reason of our belief that there is a God.

- 1. Because it is the foundation of all natural and revealed religion; and therefore it must not be received merely by tradition, as though there were no other reason why we believe it, but because others do so, or because we have been instructed herein from our childhood; for that is unbecoming the dignity and importance of the subject, and would be an instance of great stupidity, especially seeing we have so full and demonstrative an evidence thereof, taken from the whole frame of nature; in which there is nothing but what affords an argument to confirm our belief that there is a God.
- 2. There is a great deal of atheism in our hearts, by reason whereof we are prone sometimes to call in question the being, perfections, and providence of God. To which we may also add, that the Devil frequently injects atheistical thoughts into our minds; which is a great affliction to us, and renders it necessary that we should use all possible means for our establishment in this great truth.

- 3. The abounding of atheism in the world, and the boldness of many in arguing against this truth, renders it necessary that we should be able to defend it, that we may stop the mouths of blasphemers, and so plead the cause of God, and assert his being and perfections against those that deny them; as Psal. xiv. 1. The fool, who saith in his heart there is no God.
- 4. This will greatly tend to establish our faith in those comfortable truths that arise from our interest in him, and give us a more solid foundation for our hope, as excited by his promises, which receive all their force and virtue from those perfections which are implied in the idea of a God.
- 5. This will make us set a due value on his works, by which we are led to conclude his eternal power and Godhead, and so to admire him in them, Job xxxvi. 24. *Remember that thou magnify his work, which men behold.*

We shall now consider those arguments mentioned in this answer, by which the being of a God may be evinced; as,

I. From the light of nature in man, by which we understand that reason which he is endowed with, whereby he is distinguished from, and rendered superior to, all other creatures in this lower world, whereby he is able to observe the connexion of things, and their dependence on one another, and infer those consequences which may be deduced from thence. These reasoning powers, indeed, are very much sullied, depraved, and weakened, by our apostacy from God, but not wholly obliterated; so that there are some remains thereof, which are common to all nations, whereby, without the help of special revelation it may be known that there is a God.

But this either respects the principle of reasoning, which we were born with, upon the account whereof infants are called intelligent creatures; or the exercise thereof in a discursive way, in the adult, who only are capable to discern this truth, which they do more or less, in proportion to their natural capacity, as they make advances in the knowledge of other things. Now for the proof of the being of a God from the light of nature, let the following propositions be considered in their respective order.

- 1. There hath been, for many ages past, a succession of creatures in the world.<sup>[9]</sup>
- 2. These creatures could not make themselves, for that which is nothing cannot act; if it makes itself, it acts before it exists; it acts as a creator before it exists as a creature; and it must be, in the same respect, both a cause and an effect, or it must be, and not be, at the same time, than which nothing can be more absurd; therefore creatures were made by another, upon which account we call them creatures.
- 3. These creatures could not make one another; for to create something out of nothing, or out of matter altogether unfit to be made what is produced out of it, is to act above the natural powers of the creature, and contrary to the fixed laws of nature; and therefore is too great a work for a creature, who can do nothing but in a natural way, even as an artificer, though he can build an house with fit materials, yet he cannot produce the matter out of which he builds it; nor can he build it of matter unfit for his purpose, as water, fire, air, &c. All creatures act within their own sphere, that is, in a natural way: but creation is a supernatural work, and too great for a creature to perform; therefore creatures cannot be supposed to have made one another.
- 4. If it was supposed possible for one creature to make another, then superiors must have made inferiors; and so man, or some other intelligent creature, must have made the world: but where is the creature that ever pretended to this power or wisdom, so as to be called *the Creator of the ends of the earth*.
- 5. If any creature could make itself, or other creatures of the same species, why did he not preserve himself; for he that can give being to himself, can certainly continue himself in being? or why did he not make himself more perfect? Why did he make himself, and other

creatures of the same species, in such a condition, that they are always indigent, or stand in need of support from other creatures.

Or farther, supposing the creature made himself, and all other things, how comes it to pass that no one knows much of himself comparatively, or other things? Does not he that makes things understand them? therefore man could not make himself, or other creatures.

6. It follows therefore from hence, that there must be a God, who is the first cause of all things, necessarily existing, and not depending on the will of another, and by whose power all things exist; *Of him, and through him, and to him are all things*, Rom. xi. 36. *In him we live, and move, and have our being*, Acts xvii. 28.

Thus much concerning the more general method of reasoning, whereby the light of nature evinces the being of a God; we proceed,

II. To consider more particularly how the being of God may be evinced from his works. The cause is known by its effects; since therefore, as was but now observed, creatures could not produce themselves, they must be created by one who is not a creature.

Now, if there be no medium between God and the creature, or between infinite and finite, between a self-existent or underived, and a derived being; and if all creatures exist, as has been shewn, by the will and power of their Creator, and so are finite and dependent; then it follows, that there is one from whom they derived their being, and on whom they depend for all things; that is, God. This is usually illustrated by this similitude. Suppose we were cast on an unknown island, and there saw houses built, but no men to inhabit them, should we not conclude there had been some there that built them? Could the stones and timber put themselves into that form in which they are? Or could the beasts of the field build them, that are without understanding? Or when we see a curious piece of workmanship, as a watch, or a clock, perform all its motions in a regular way, can we think the wheels came together by chance?<sup>[10]</sup> should we not conclude that it was made by one of sufficient skill to

frame and put them together in that order, and give motion to them? Shall the clay say to him that fashioned it, What makest thou, or thy work, He hath no hands? Isa. xlv. 9.

This leads us to consider the wisdom of God in his works, which demonstrates his being. This the Psalmist mentions with admiration, Psal. civ. 24. *O Lord, how manifold are thy works; in wisdom hast thou made them all!* When we see letters put together, which make words or sentences, and these a book, containing the greatest sense, and the ideas joined together in the most beautiful order, should we not conclude that some man, equal to this work, had put them together? Even so the wisdom that shines forth in all the parts of the creation, proves that there is a God. This appears,

In the exact harmony and subserviency of one part of the creation to another, Hos. ii. 21, 22. I will hear, saith the Lord; I will hear the heavens, and they shall hear the earth. And the earth shall hear the corn, and the wine, and the oil, and they shall hear Jezreel. One part of this frame of nature ministers to another. Thus the sun, and other heavenly bodies, give light to the world, which would be no better than a cave or dungeon without them; and afford life and influence to plants and trees; and maintain the life of all living creatures. The clouds send down rain that moistens the earth, and makes it fruitful; and this is not poured forth by whole oceans together, but by small drops, Job xxxvi. 27. He maketh small the drops of water; they pour down rain according to the vapour thereof; and these are not perpetual, for that would tend to its destruction. The moist places of the earth, and the sea supply the clouds with water, that they may have a sufficient store to return again to it. The air fans and refreshes the earth, and is necessary for the growth of all things, and the maintaining the life and health of those that dwell therein. This subserviency of one thing to another is without their own design or contrivance; for they are not endowed with understanding or will; neither doth this depend on the will of the creature. The sun doth not enlighten or give warmth to the world, or the clouds or air refresh the earth at our pleasure; and therefore all this is subject to the order and direction of one who is the God of nature, who

commands the sun, and it shineth, and the clouds to give rain at his pleasure. It is he that gave the regular motion to the heavenly bodies, and, by his wisdom, fixed and continues the various seasons of the year, summer and winter, seed-time and harvest, day and night, and every thing that tends to the beauty and harmony of nature; therefore these curious, and never-enough to be admired, works, plainly declare that there is a God. This is described with unparalleled elegancy of style, Job xxxvii. 9, &c. Out of the south cometh the whirlwind; and cold out of the north. By the breath of God, frost is given; and the breadth of the waters is straitened. Also by watering he wearieth the thick cloud; he scattereth his bright cloud. Dost thou know the balancings of the clouds, the wondrous works of him which is perfect in knowledge? How thy garments are warm when he quieteth the earth by the south-wind?<sup>[11]</sup>

But that we may farther evince this truth, we shall lay down the following arguments to prove the being of a God, which appears,

- I. From those creatures that are endowed with a lower kind of life than man.
- 1. No creature can produce a fly or the least insect, but according to the fixed laws of nature; and that which we call life, or the principle of their respective motion and actions, none but a God can give; so that his being is plainly proved, from all living creatures below man, which are subservient, many of them, to one another, and all to man, and that not by our ordering; therefore this is done by the hand of him who is the God of nature.
- 2. The natural instinct of living creatures, every one acting according to its kind; and some of the smallest creatures producing things that no human art can imitate, plainly proves a God. Thus the bird in building its nest; the spider in framing its web; the bee in providing store-houses for its honey; and the ant in those provisions which it lays up in summer against winter; the silk-worm in providing cloathing for man, and in being transformed into various shapes, and many others of smaller sort of creatures, that act in a wonderful

way, without the exercise of reason or design, these all prove the being of God.

- 3. The greater, fiercer, or more formidable sort of living creatures, as the lion, tiger, and other beasts of prey, are so ordered, that they fly from man, whom they could easily devour, and avoid those cities and places where men inhabit, that so we may dwell safely. They are not chased into the woods by us; but these are allotted, as the places of their residence by the God of nature.
- 4. Those living creatures that are most useful to men, and so subject to them, *viz.* the horse, camel, and many others, these know not their own strength, or power, to resist or rebel against them; which is ordered by infinite wisdom: and there are many other instances of the like nature, all which are very strong arguments to prove that there is a God, whose glory shines forth in all his works.
- II. From the structure of human bodies, in which respect we are said to be fearfully and wonderfully made; this, if it be abstractedly considered without regard to the fixed course and laws of nature, exceeds the power and skill of all creatures, and can be no other than the workmanship of a God, and therefore is a demonstration of his being and perfections. No man ever pretended to give a specimen of his skill therein. The finest statuaries or limners, who have imitated or given a picture, or representation of human bodies, have not pretended to give life or motion to them; herein their skill is baffled. The wisest men in the world have confessed their ignorance of the way and manner of the formation of human bodies; how they are framed in their first rudiments, preserved and grow to perfection in the womb, and how they are increased, nourished, and continued in their health, strength, and vigour for many years. This has made the inquiries of the most thoughtful men issue in admiration: herein we plainly see the power and wisdom of God, to which alone it is owing.

Here it may be observed, that there are several things very wonderful in the structure of human bodies, which farther evince this truth. As,

- 1. The organs of sense and speech.
- 2. The circulation of the blood, and the natural heat which is preserved for many years together, of which there is no instance but in living creatures. Even fire will consume and waste itself by degrees, and all things, which have only acquired heat, will soon grow cold; but the natural heat of the body of man is preserved in it as long as life is continued.
- 3. The continual supply of animal spirits, and their subserviency to sense and motion. [13]
- 4. The nerves, which, though small as threads, remain unbroken, though every one of these small fibres performs its office, and tends to convey strength and motion to the body.
- 5. The situation of the parts in their most proper place: the internal parts, which would be ruined and destroyed if exposed to the injuries that the external ones are: these are secured in proper inclosures, and so preserved, Job x. 11. Thou hast cloathed me with skin and flesh, and hast fenced me with bones and sinews.
- 6. All the parts of the body are so disposed, that they are fitted for their respective uses, as being situate in those places which render them most fit to perform their proper actions.
- 7. The differing features of different bodies, so that we scarce see persons in all respects alike, is wonderful, and the result of divine wisdom: for even this is necessary for society, and our performing the duties we owe to one another.
- 8. The union of this body with the soul, which is a spirit of a very different nature, can never be sufficiently admired or accounted for; but gives us occasion herein to own a superior, infinitely wise being. Which leads us,
- III. To consider how the being of God may be evinced from the nature of the soul of man. He is said, Zech. xii. 1. *To have formed the spirit of man within him.* And hereby his power and wisdom, and consequently his being, is declared. For,

1. The nature of a spiritual substance is much less known than that of bodies; and therefore that which we cannot fully understand, we must admire.

If the wisdom and power of God is visible in the structure of our bodies, it is much more so in the formation of our souls; and since we cannot fully describe what they are, and know little of them but by their effects, certainly we could not form them; and therefore there is a God, who is the *Father of spirits*.

- 2. The powers and capacities of the soul are various, and very extensive.
- (1.) It can frame ideas of things superior to its own nature, and can employ itself in contemplating and beholding the order, beauty, and connexion of all those things in the world, which are, as it were, a book, in which we may read the divine perfections, and improve them to the best purposes.
- (2.) It takes in the vast compass of things past, which it can reflect on and remember, with satisfaction, or regret: and it can look forward to things to come, which it can expect, and accordingly conceive pleasure or uneasiness in the forethoughts thereof.
- (3.) It can chuse or embrace what is good, or fly from and reject what is evil and hurtful to it.
- (4.) It is capable of moral government, of conducting itself according to the principles of reason, and certain rules enjoined it for the attaining the highest end.
- (5.) It is capable of religion, and so can argue that there is a God, and give him the glory that is due to his name, and be happy in the enjoyment of him.
- (6.) It is immortal, and therefore cannot be destroyed by any creature; for none but God has an absolute sovereignty over the spirits of men; *No man hath power over the spirit to retain the spirit; neither hath he power in the day of death,* Eccles. viii. 8.

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